

**THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of:

GYOBU et al.

Application No.: 10/049,438

Group Art Unit: 1713

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For: A POLYESTER POLYMERIZATION CATALYST, POLYESTER
PRODUCED BY USING THE SAME, AND A PROCESS FOR
PRODUCING POLYESTER

DECLARATION UNDER 37 C.F.R. §1.132

Mail Stop RCE
Commissioner of Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Shoichi GYOBU, hereby declare and state:

THAT I am a citizen of Japan;

THAT I have received a degree of Master of Engineering in 1993 from Kyoto
University;

THAT I have been employed by Toyo Boseki Kabushiki Kaisha since 1993,
where I hold a position as a researcher, with responsibilities in the development of
polymerization catalysts for polyester preparation;

THAT I am one of the inventors of the above-identified application and I am
familiar with the subject matter thereof; and

THAT I have read the Office Action mailed and the references cited therein
and am familiar with the subject matter thereof.

I further declare and state that the following experiments, performed by me
or under my direction or supervision, show that the catalysts of the present

invention can achieve unexpected results compared with the closest catalysts disclosed in the prior art references, Jackson (U.S. Patent No. 3,847,873; hereinafter referred to as "Jackson") and Ridland (WO 99/28033; hereinafter referred to as "Ridland"), relied upon by the Office Action.

Examples 1-10

Experiments of Examples 1 to 10 were carried out each using a polymerization catalyst that falls within the scope of the pending claims. Each of the polymerization catalysts used in Experiments 1 to 10 comprised an aluminum compound (aluminum compounds Al1, Al2 and Al3 shown in Table 1 attached) and an aromatic phosphorus compound (aromatic phosphorus compounds P1, P2, P3, P4, and P5 shown in Table 1) in the combinations shown in Table 1, i.e.,

- Example 1: aluminum acetylacetonate and diethyl 3,5-di-*tert*-butyl-4-hydroxy benzylphosphonate;
- Example 2: aluminum acetate, basic and diethyl 3,5-di-*tert*-butyl-4-hydroxy benzylphosphonate;
- Example 3: aluminum chloride and diethyl 3,5-di-*tert*-butyl-4-hydroxy benzylphosphonate;
- Example 4: aluminum acetylacetonate and diphenylphosphinic acid;
- Example 5: aluminum acetate, basic and diphenylphosphinic acid;
- Example 6: aluminum chloride and diphenylphosphinic acid;
- Example 7: aluminum acetylacetonate and diethyl benzylphosphonate;
- Example 8: aluminum acetate, basic and diethyl benzylphosphonate;
- Example 9: aluminum acetylacetonate and diethyl 1-naphthylmethylphosphonate; and
- Example 10: aluminum acetylacetonate and diethyl 4-phenylbenzylphosphonate.

Example 11

Similarly, an experiment was conducted in Example 11 using a polymerization catalyst that is not a polymerization catalyst of any of the currently pending claims. But it is a polymerization catalyst according to the claims

pending in the application when filed up to before the claims were amended by the Amendment filed on September 21, 2004. The polymerization catalyst used in Example 11 contained an aluminum substance and an aromatic phosphorus compound, with aluminum tri-sec-butoxide as a representative of an aluminum alkoxide and with diethyl 3,5-di-tert-butyl-4-hydroxy benzylphosphonate as a representative of the aromatic phosphorus compound. The aluminum substance, aluminum tri-sec-butoxide, was used in a esterification catalyst of Ridland's Example 12 (please see Table 1 attached). Thus, the polymerization catalyst used in Example 11 comprises a combination of substances shown below.

Example 11: aluminum tri-sec-butoxide and diethyl
 3,5-di-tert-butyl-4-hydroxy benzylphosphonate

Comparative Examples 1-4

Four Comparative Examples are described below for comparison with the above Examples of the invention.

A similar experiment was performed in Comparative Example 1 using a polymerization catalyst comprising an aluminum compound and a non-aromatic phosphorus compound used in Example 6 of Jackson. However, since diethyl hexadecylphosphonate, the non-aromatic phosphorus compound used in Example 6 of Jackson, was not commercially available in Japan, diethyl hexadecylphosphonate was replaced with another alkyl phosphonate, dimethyl octadecylphosphonate, in Comparative Example 1 (please see Table 1 attached).

A similar experiment was performed in Comparative Examples 2 and 4 using a polymerization catalyst comprising an aluminum compound and a non-aromatic phosphorus compound used in Example 12 of Ridland. Comparative Example 4 differs from Comparative Example 2 in including sodium, added as sodium hydroxide, in the polymerization catalyst (please see Table 1 attached).

A similar experiment was also performed in Comparative Example 3 using a polymerization catalyst comprising zinc acetate used in Example 3 of Jackson, and an aromatic phosphinic acid compound similar to the ethyl bis(p-biphenyl)phosphinate used in Example 3 of Jackson (please see Table 1 attached). Because the ethyl bis(p-biphenyl)phosphinate used in Example 3 of

Jackson was not commercially available in Japan, instead diphenylphosphinic acid was used in Comparative Example 3.

Therefore, the polymerization catalysts used in Comparative Examples 1-4 comprise the following combinations of substances:

Comparative Example 1: aluminum acetylacetonate and dimethyl octadecylphosphonate;

Comparative Example 2: aluminum tri-sec-butoxide and butyl phosphate;

Comparative Example 3: zinc acetate and diphenylphosphinic acid; and

Comparative Example 4: aluminum tri-sec-butoxide, butyl phosphate and sodium hydroxide.

The amounts of the catalysts used in Comparative Examples 1-4 were according to the disclosures in Example 6 of Jackson, Example 3 of Jackson or Example 12 of Ridland. In particular, the molar ratio of the metal atoms and the phosphorus atoms in the catalysts used in Examples 6 of Jackson, Example 3 of Jackson or Example 12 of Ridland was also used in the Comparative Examples 1-4.

In each of Examples and Comparative Examples, terephthalic acid and ethylene glycol underwent esterification in an esterification reactor followed by polycondensation in a polycondensation reactor. The polycondensation was performed with stirring coupled with monitoring of the stirring torque. At the start of the polycondensation reaction, the stirring torque was 1.3 N·m, which was gradually increased as the polycondensation reaction progressed reflecting an increase in melt viscosity as the molecular weight of the polyester produced became higher. The polycondensation reaction with stirring was stopped when the sooner of one of two alternative conditions was met: (a) the torque of stirring reached a target torque of 3.8 N·m, in which case the time to reach the target torque was noted; and (b) the stirring lasted 180 minutes and yet the torque of stirring had not reached the target torque. The target torque was set at a value based on the experience of applicants, which value would yield polyester of optimal intrinsic viscosity. The intrinsic viscosity (IV) of the polyester produced was measured at a temperature of 30°C with an Ostwald viscometer in a mixed

solvent of phenol/1,1,2,2-tetrachloroethane (6/4 in weight ratio). Strands of the polyester produced were obtained from the polycondensation reactor at the termination of the polycondensation. The transparency of the polyester strands produced was also noted via visual observation.

Example 1

The polymerization reactor used was composed of an esterification reactor and a polycondensation reactor each with a volume of 10 L. In the esterification reactor, 2594 g of terephthalic acid and 1163 g of ethylene glycol were allowed to react when heated to 260°C with stirring and the removal of water vapor formed during esterification to give an esterification product. Based on the amount of the terephthalic acid component, 0.015 mol% of aluminum acetylacetonate (i.e., 21 ppm in terms of the aluminum atom) and 0.022 mol% of diethyl 3,5-di-*tert*-butyl-4-hydroxy benzylphosphonate (i.e., 36 ppm in terms of the phosphorus atom) were added as a polymerization catalyst in the form of an ethylene glycol solution to the esterification product, and then transferred to the polycondensation reactor.

In the polycondensation reactor, the temperature of the esterification product was raised from 260°C to 280°C over one hour, while the pressure was reduced from atmospheric pressure to 80 Pa. The polycondensation reaction was allowed to proceed with stirring under a pressure of 80 Pa at a temperature of 280°C.

At a polycondensation reaction time of 34 minutes, the target stirring torque of 3.8 N·m was reached, and thus the polycondensation reaction was stopped. The resulting polyester had an intrinsic viscosity of 0.624 dl/g. The results are shown in Table 1. The transparency, or a lack thereof (if any), of the polyester produced was determined upon visual inspection with naked eyes (please see Table 2).

Examples 2 to 11

Experiments were performed using the process of Example 1 except that the polymerization catalysts shown in Table 1 and described above were used. In

each of Examples 4 to 6, diphenylphosphinic acid was added in the form of a solid, because it was insoluble in ethylene glycol. In Example 4, when the target stirring torque of 3.8 N·m was not reached even at a polycondensation reaction time of 180 minutes, the polycondensation reaction was stopped. In Examples 2, 3 and 5-11, when the target stirring torque of 3.8 N·m was reached during the polycondensation reaction before 180 minutes, the polycondensation reaction was stopped and the duration of the polycondensation reaction was recorded. The intrinsic viscosities of the polyester produced were measured. The results are shown in Table 1. The transparency, or a lack thereof (if any), of the polyesters produced as determined upon visual inspection with naked eyes was noted (please see Table 2).

Comparative Examples 1-4

The catalysts shown in Table 1 and as described above were used and experiments were performed using the process of Example 1 except as described below.

In Comparative Example 1, 0.016 mol% of aluminum acetylacetonate (i.e., 23 ppm in terms of aluminum atom) and 0.028 mol% of dimethyl octadecylphosphonate (i.e., 45 ppm in terms of phosphorus atom) were used in the polymerization catalyst (please see Table 2).

In Comparative Example 2, 0.117 mol% of aluminum tri-sec-butoxide (i.e., 164 ppm in terms of aluminum atom) and 0.058 mol% of butyl phosphate (i.e., 94 ppm in terms of phosphorus atom) were used in the polymerization catalyst (please see Table 2).

In Comparative Example 3, the amount ratio of the zinc atom (as zinc acetate) and the phosphorus atom (as diphenylphosphinic acid in Comparative Example 3) used in Jackson's Example 3 was reproduced in Comparative Example 3. Thus, 217 ppm of the zinc atom from zinc acetate and 205 ppm of the phosphorus atom from diphenylphosphinic acid were used in the polymerization catalyst in Comparative Example 3 (see Table 2).

In Comparative Example 4, the same amounts of aluminum tri-sec-butoxide and butyl phosphate were used as in Comparative Example 2 but sodium

hydroxide was added, so that 164 ppm in terms of aluminum atom, 140 ppm in terms of sodium atom, and 94 ppm in terms of phosphorus atom were used in the polymerization catalyst of Comparative Example 4 (please see Table 2).

Since the target torque of 3.8 N·m was not reached even at a polycondensation reaction time of 180 minutes with Comparative Examples 1, 2 and 3, the polycondensation reaction was stopped. With Comparative Example 4, the target torque of 3.8 N·m was reached at a polycondensation reaction time of 39 minutes, when the polycondensation reaction was stopped. The intrinsic viscosities of the polyesters produced in Comparative Examples 1-4 were measured. The results are shown in Table 1. The transparency, or a lack thereof, of the polyesters produced as determined upon visual inspection with naked eyes was noted (please see Table 2).

Results

Table 1 shows that when the aluminum compound and the phosphorus compound were used as catalysts in the combination according to the invention, except for Example 4, the target stirring torque was reached before the lapse of a polycondensation reaction time of 180 minutes (at 34-137 minutes in Examples 1-3 and 5-11), and the intrinsic viscosity of the resulting polyester was 0.601-0.642 dl/g, which met the requirement of at least 0.55 dl/g acceptable according to the skilled in the art. For instance, H. Ludewig disclosed in *Polyester Fibres Chemistry and Technology* that spinnable technical grand polyethylene terephthalate (PET) has an intrinsic viscosity of 0.55-0.65 (see the last paragraph of page 129; Wiley-Interscience, John Wiley & Sons, 1971, which is attached).

In Example 4, the polycondensation conducted for the full 180 minutes did not reach the target torque, but the polyester produced had an intrinsic viscosity of 0.573 dl/g (see Table 1), which still met the requirement of at least 0.55 dl/g for spinnable polyethylene terephthalate.

In Comparative Examples 1-3, the target stirring torque was not reached after 180 minutes of polycondensation reaction and the intrinsic viscosity of the resulting polyester was less than 0.50 dl/g, which is not a satisfactory level for

polyesters.

In Comparative Example 4, the target torque was reached in 39 minutes of polycondensation reaction and the resulting polyester had an intrinsic viscosity of 0.608. However, the polyester produced in Comparative Example 4 was hazy. The polyesters produced in Comparative Examples 1-3 were also hazy (please see Table 2 attached).

The data on the intrinsic viscosity and polycondensation reaction time are also presented in an attached graph, plotting intrinsic viscosity versus polycondensation reaction time of Examples 1-11 (drawn with solid lines) and Comparative Examples 1-4 (drawn with dashed lines). The graph pictorially shows the differences between Examples 1-11 and Comparative Examples 1-3.

Also attached is a sheet having 9 pictures comparing the "transparency" of the polyesters produced in Comparative Example 1 (labeled as "Con 1 (J)"), Comparative Example 4 (labeled as "Con 4 (Na)_R") and Examples 1-10 (labeled as "Ex. 1", "Ex. 2", "Ex. 3", etc.). In each of the 9 pictures, the polyester strands produced in Comparative Example 4 were laid side by side with the polyester strands produced in some of the Examples 1-10, except that in the right picture in the bottom row the polyester strands produced in Comparative Example 1 were included for comparison. The 9 pictures show that the polyester strands produced in Example 1-10 were transparent and clear so that, even though the polyester strands actually extended horizontally from the left side to the right side of the pictures, one could barely discern a faint outline, or could not even discern any outline, in some portions of the polyester strands of Examples 1-10 in the 9 pictures. In contrast, the polyester strands produced in Comparative Example 4 were hazy. The polyester strands produced in Comparative Example 1 were both being hazy and having bubbles inside.

The duration it takes to reach the target torque in the polycondensation reaction reflects how effective the polymerization catalyst in catalyzing the polymerization, in which a shorter duration generally means higher effectiveness. The duration was more than 180 minutes in Comparative Examples 1-3 and between 34 and 137 minutes in Examples 1-3 and 5-11. The results on the polycondensation reaction time show that the polymerization catalysts used in

Comparative Examples 1, 2 and 3 were much less effective in catalyzing the polycondensation than the polymerization catalysts used in Examples 1-3 and 5-11. These results were obtained although the amount of the polymerization catalyst used was higher in each of Comparative Examples 1-3 than in each of Examples 1-11 of the invention. The higher effectiveness of the polymerization catalysts of Examples 1-3 and 5-11 than that of the polymerization catalysts of Comparative Examples 1-3 is an unexpected result based on what has been known in the prior art.

Like Comparative Examples 1-3, Example 4 had a polycondensation reaction time of 180 minutes. However, with an intrinsic viscosity 0.573 dl/g, i.e., higher than the minimal acceptable limit of 0.55 dl/g, the polyester produced by the polymerization catalyst of Example 4 would be spinnable, while the polyesters produced by the polymerization catalysts of Comparative Examples 1-3 would not be spinnable as reflected by intrinsic viscosities of 0.412-0.483 dl/g which were much lower than the minimal acceptable limit of 0.55 dl/g. Spinnability is a required quality for polyester to be used in making polyester fibers. Thus, the polymerization catalyst of Example 4 produced polyester acceptable for making polyester fibers, while the polymerization catalysts of Comparative Examples 1-3 produced polyester unacceptable for making polyester fibers. The ability of the polymerization catalyst of Example 4 to produce polyester that was spinnable, while the inability of the polymerization catalysts of Comparative Examples 1-3 to produce polyester that was spinnable is an unexpected result based on what has been known in the prior art.

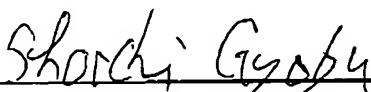
The polymerization catalysts of Comparative Examples 1-4 produced hazy polyester, while the polymerization catalysts of Examples 1-11 produced polyester that was transparent and clear. Haziness is undesirable in polyester limiting the commercial applicability of the polyester. The ability of the polymerization catalysts of Examples 1-11 to produce transparent and clear polyester in contrast with the ability of polymerization catalysts of Comparative Examples 1-4 to produce only hazy polyester is an unexpected result based on what has been known in the prior art.

From the above, it is concluded that the polymerization catalysts according

to the claimed invention unexpectedly possess significantly higher and/or better catalyst activities than the closest catalysts of Jackson and Ridland.

I declare further that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

Signed:



Shoichi GYOBU

Date: The 9th Day of August, 2006

Attachments:

Table 1 entitled "Results of Experiments";

Table 2 entitled "Experimental Conditions";

A graph plotting intrinsic viscosity versus polycondensation reaction time;

A sheet of 9 pictures; and

H. Ludewig, *Polyester Fibres Chemistry and Technology*, page 129;

Wiley-Interscience, John Wiley & Sons, 1971.

Results of Experiments

Table 1

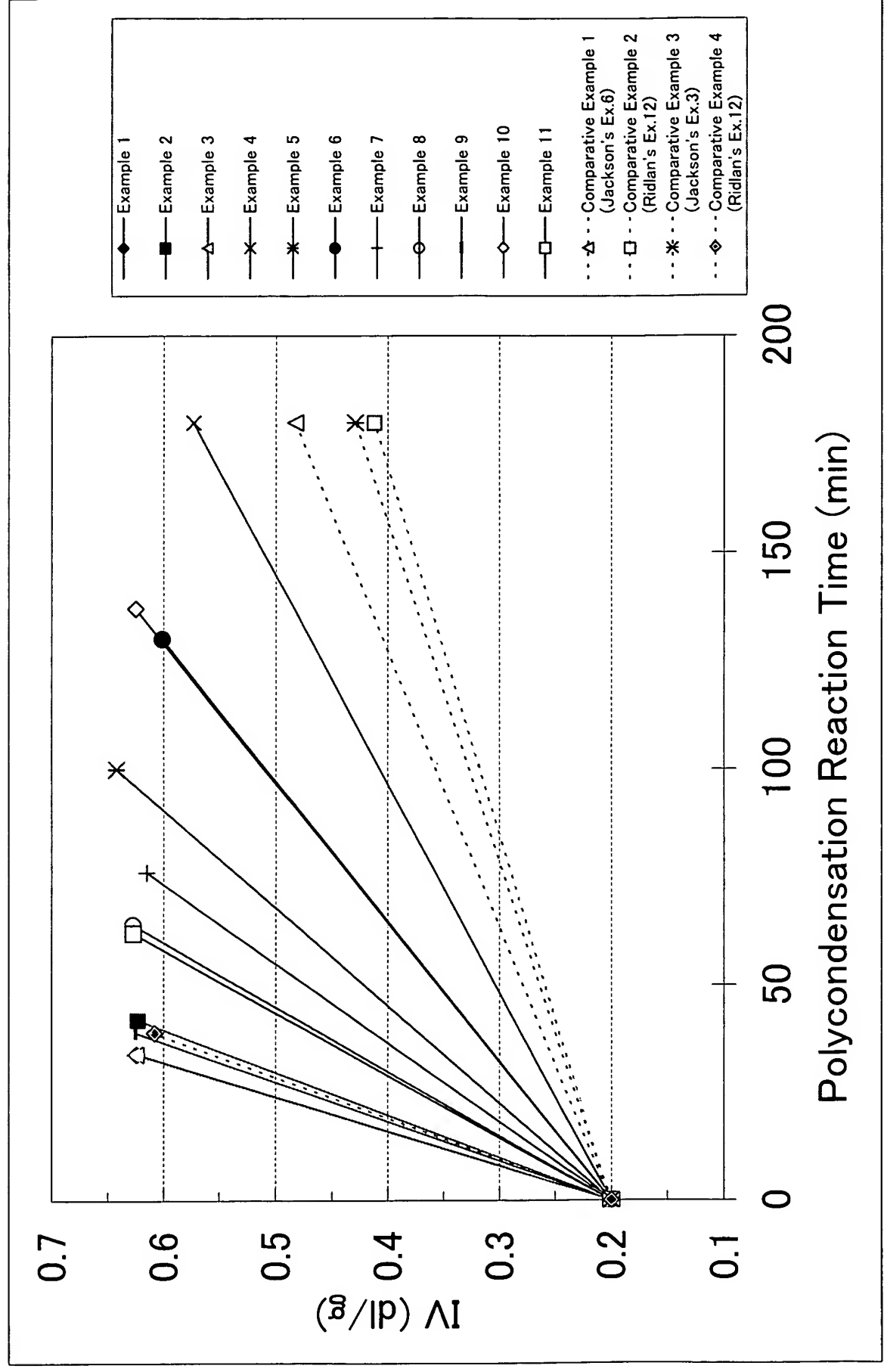
	P1	P2	P3	P4	P5	Jackson's Ex. 6 P	Ridland's Ex. 12 P	Ridland's Ex. 12 P + Na
Upper: Polycondensation Reaction Time (min) Lower: IV (dl/g)	[Irganox1222] Diethyl 3,5-di- <i>tert</i> - butyl-4-hydroxy benzylphosphonate	[Diphe-Ph(A)] Diphenylphosphinic acid	[BPDE] Diethyl benzylphosphonate	[NMPDE] Diethyl 1-naphthylmethyl phosphonate	[DEBIP] Diethyl 4- phenylbenzyl phosphonate	[C18PDM] Dimethyl octadecylphosphonate	[TBPA] Butyl phosphate	[TBPA + NaOH] Butyl phosphate + Sodium hydroxide
Al1 [Al(acac)3] Aluminum acetylacetonate	Example 1 34 0.624	Example 4 180 0.573	Example 7 76 0.615	Example 9 39 0.625	Example 10 137 0.625	Comparative Example 1 180 0.483	-	-
Al2 [Al(OH)(ac)2] Aluminum acetate, basic	Example 2 42 0.623	Example 5 100 0.642	Example 8 64 0.627	-	-	-	-	-
Al3 [AlCl3] Aluminum chloride	Example 3 34 0.625	Example 6 130 0.601	-	-	-	-	-	-
Ridland's Ex. 12 Al [Al(OBu)3] Aluminum tri- <i>sec</i> -butoxide	Example 11 62 0.627	-	-	-	-	-	Comparative Example 2 180 0.412	Comparative Example 4 39 0.608
Jackson's Ex. 3 Zn [Zn(ac)2] Zinc acetate	-	Comparative Example 3 180 0.429	-	-	-	-	-	-



Experimental Conditions

Table 2

	Examples 1-11 (Invention)	Comp. Ex.1 (Jackson Ex.6)	Comp. Ex.2 (Ridland Ex.12)	Comp. Ex.3 (Jackson Ex.3)	Comp. Ex.4 (Ridland Ex.12)
Catalyst	Al / P	Al / P	Al / P	Zn / P	Al / Na / P
(atom amount ratio)	21ppm / 36ppm	23ppm / 45ppm	164ppm / 94ppm	217ppm / 205ppm	164ppm / 140ppm / 94ppm
TPA / EG amount ratio	Same	Same	Same	Same	Same
Polycondensation Time (min.)	34 - 180	180	180	180	39
Temperatures	Same	Same	Same	Same	Same
Pressures	Same	Same	Same	Same	Same
Esterification Reactor	Same	Same	Same	Same	Same
Polycondensation Reactor	Same	Same	Same	Same	Same
PET					
intrinsic viscosity (dl/g)	0.573 - 0.642	0.483	0.412	0.429	0.608
PET					
Transparency	Clear	Hazy	Hazy	Hazy	Hazy



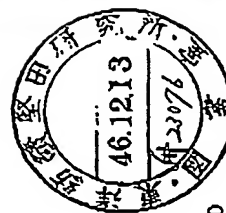
Polyester Fibres

Chemistry and Technology

Hermann Ludwig

*with the collaboration of
Werner Roth, Ernst Littmann, Liselotte Fuller,
Reinhold Eppendorfer and Hans Richardt
all at VEB Chemiefaserwerk Schwarz, 'Wilhelm Pieck',
Rudolstadt/Thüringen*

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Fibres Research Association, Shirley Institute, Manchester,
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from Dr. David M. Jones.*



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Preface

It is well known that, in 1928-1937, W. H. Carothers laid the scientific foundation for the production of melt-spun fibres such as polyamide and polyester fibres. During this period the first polyamide filaments were spun also in Germany, from polymer melts produced from *o*-aminononanoic acid; those represented a modification of the patents granted to W. H. Carothers. Even a beginner can carry out the polycondensation of *o*-aminononanoic acid or *o*-aminoundecanoic acid—at least in the laboratory; however, polycondensation of linear polyesters, which Carothers had also investigated by the use of molecular distillation, is difficult. For this reason, chemists dealing with fibrous substances in the 1930s preferred research on polyamides rather than on polyesters, especially since, in 1938, P. Schlack succeeded in replacing the nylon 66 process (which also presents difficulties) by the much simpler caprolactam process.

Credit is due to the English research workers J. R. Winfield and J. T. Dickson on the one hand and the inventor of the caprolactam polyamide fibre, P. Schlack, on the other in that they placed Carothers' polyester process on an economically practicable basis by using terephthalic acid as the dicarboxylic acid component for the synthesis of the linear polyester. The author has participated in the tempestuous development of polyamides, polyurethanes, and polyesters during the last three decades and, in close collaboration with P. Schlack, F. Wenger, and H. Klare, played a leading part in the further development of these melt-spun fibres.

Initially, it was intended to publish this book within the framework of the second edition of H. Klare's *Synthetische Fasern aus Polyamiden*. However, since there are essential differences between polyamides and polyesters—especially as regards their chemistry, characteristics, and applicability—it was decided to publish both books separately.

The writer was fortunate in securing, as co-authors, experts who have long-standing experience and comprehensive knowledge in their specialized fields and who are intimately involved in the development of polyester fibres. For instance, the physicochemical problems arising in Chapters 2, 5, 6, and 7 and questions of setting and finishing (Chapter 11) were in the main

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FAND [77] derived formula (10) from the HUGGINS equation (6) after ascertaining the constant K for polyethylene terephthalate.

GAZEHL and NEURZ ascertained the molecular weight by means of end-group determination. Determination of the terminal OH groups of polyester was carried out in two different ways, by acetylation with bromoacetyl bromide or by reaction with phenylisocyanate which gives diurethanes.

Since the determination of molecular weights by the end-group method result in the number average \bar{M}_n , whereas the viscometric method yields the weight average \bar{M}_w , fractionated material was used for the tests. This was produced according to GORDVUKO's method [78] and embraced molecular weights ranging from 5,000–25,000. Correspondence between weight average and number average molecular weights can be achieved only with molecularly uniform products.

The two independent methods which were used to obtain the end-group molecular weights gave rather good agreement, the margin of error being about 10%.

A comparison between the viscometric results and the end-group molecular weights enabled GAZEHL and NEURZ to derive the following viscosity-molecular weight relationship with modification of Equation (5):

$$[\eta] = 0.9 \times 10^{-4} \bar{M}^{0.47} \quad (11)$$

Equation (11) conveys the dependence of the limiting viscosity on the molecular weight of fractionated polyester, on condition that the viscosity is determined in phenol-acetylene tetrachloride (1:1) at 20°C; it is approximately valid in the molecular weight range between 5,000 and 25,000.

Spinnable, but not fractionated, technical polyethylene terephthalate has a relative viscosity—measured in phenol-acetylene tetrachloride at a concentration of 0.5%—of at least 1.3–1.36 [76] and therefore, according to Equation (10), a basis viscosity $[\eta]$ equalling 0.55–0.65. This results, arithmetically, by Equation (11) in a molecular weight \bar{M}_w of 23,000–27,000 (weight average). Furthermore, so as to establish the number average molecular weight \bar{M}_n , GAZEHL and NEURZ applied both methods to the end-group determination of non-fractionated polyester. By comparing the results, which were ascertained in the molecular weight range between 6,000 and 25,000, with the corresponding basis viscosity $[\eta]$, they were able to derive the relation

$$[\eta] = 1.27 \times 10^{-4} \bar{M}^{0.55} \quad (12)$$

for non-fractionated material. In accordance with these findings, the molecular weight \bar{M}_n of spinnable technical polyester, having the relative viscosity of 1.30–1.36 mentioned above, lies between 16,000 and 20,000 (number average).

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molecular weight of macromolecular substances the mean molecular weight is derived, by the application of one or the other method as a number average \bar{M}_n or as a weight average \bar{M}_w .

The 'calibration' of the viscometric method, which does not represent an absolute technique of determining molecular weight, is carried out, as already mentioned, by comparison with an absolute weight determination. This relationship between viscosity and molecular weight as to be established separately for each macromolecular product and each solvent used.

TURSKA-KOSMATEZ and SKWARSKI [76] have compared the results from viscometric measurements—the viscosity of which was ascertained in 0.5% solution in pure phenol at 50°C—with molecular weights obtained cryoscopically and postulated the following relationship for polyethylene terephthalate based on Equation (5):

$$[\eta] = 5.517 \times 10^{-4} \bar{M}^{0.70} \quad (8)$$

where \bar{M} = molecular weight.

Cryoscopic methods cannot be used with these higher molecular weights, since such determination can be carried out only up to a molecular weight maximum of 3,600. However, this value is far below the molecular weight of spinnable polyesters. An extrapolation on the established curve in this region is of doubtful value.

MARSHALL and TODD [51] postulate the following equation for polyethylene terephthalate:

$$[\eta] = 5.66 \times 10^{-4} \bar{M}^{0.73} \quad (9)$$

These authors performed their measurements with *o*-chlorophenol as solvent at a temperature of 25°C and obtained the molecular weights required for the comparison by ascertaining the osmotic pressure. However, the osmotic method is safe only in the higher range of molecular weights and the difficulties connected with this method can be regarded as the cause of the wide scattering of the observed values. This scattering naturally influences the precision of the last results.

It was left to GAZEHL and NEURZ [76] to establish the viscosity-molecular weight relationship of polyethylene terephthalate for spinnable products. Viscosity measurements are carried out with a mixture of phenol and tetrachloroethane (1:1) at 20°C. The limiting viscosity $[\eta]$ was calculated on the basis of the equation

$$[\eta] = \frac{\sqrt{1 + 1.4\eta_{sp}} - 1}{0.35} \quad (10)$$

using the specific viscosity η_{sp} measured with a 0.5% solution.